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FSc / ICS Part-II Chemistry — Punjab Board

CHAPTER 12

Aldehydes and Ketones

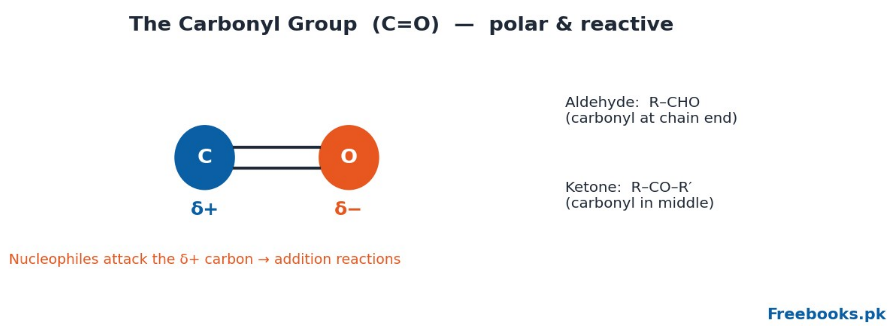

Figure 12.1 — The polar carbonyl group (C=O) is the reactive centre of aldehydes and ketones.

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1. Chapter Overview

Aldehydes and ketones both contain the carbonyl group (C=O). In an aldehyde the carbonyl carbon is at the end of the chain and carries a hydrogen (R–CHO), while in a ketone it is in the middle, joined to two carbon groups (R–CO–R′). The carbonyl group is polar, with a δ+ carbon and a δ− oxygen, which makes these compounds react readily with nucleophiles. Aldehydes and ketones are important in the manufacture of plastics, perfumes, medicines and solvents (for example methanal in Bakelite and acetone as a solvent). A central theme of this chapter is how to tell aldehydes and ketones apart.

2. Learning Objectives

- Identify the carbonyl group and distinguish aldehydes from ketones.
- Describe methods of preparing aldehydes and ketones.
- Explain nucleophilic addition reactions of the carbonyl group.
- Describe the oxidation and reduction of aldehydes and ketones.
- Use Tollens', Fehling's, Benedict's and the iodoform tests to distinguish them.
- State the important uses of methanal and acetone.

3. Key Concepts

3.1 The Carbonyl Group

The carbonyl group, C=O, is the functional group of both aldehydes and ketones. Because oxygen is more electronegative than carbon, the group is polar: the carbon carries a partial positive charge (δ+) and the oxygen a partial negative charge (δ−). The δ+ carbon is therefore open to attack by nucleophiles, which is why nucleophilic addition is the characteristic reaction of these compounds.

3.2 Preparation

Aldehydes and ketones are most simply prepared by the controlled oxidation of alcohols: oxidising a primary alcohol gives an aldehyde, and oxidising a secondary alcohol gives a ketone. They can also be made by the ozonolysis of alkenes and by other routes. Methanal and ethanal are made industrially from methanol and ethene.

3.3 Nucleophilic Addition Reactions

The typical reaction of the carbonyl group is nucleophilic addition, in which a nucleophile adds to the δ+ carbon and the π-bond of C=O opens. Important examples include addition of hydrogen cyanide (HCN) to give cyanohydrins, addition of sodium hydrogen sulphite ($NaHSO_3$) to give crystalline bisulphite compounds (useful for purification), and addition of Grignard reagents (which, after hydrolysis, give alcohols). Aldehydes are generally more reactive towards these additions than ketones, because ketones have two bulky groups that hinder the approach of the nucleophile.

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3.4 Oxidation and Reduction

Aldehydes and ketones behave very differently towards oxidation. Aldehydes are easily oxidised to carboxylic acids (because the carbonyl carbon carries a hydrogen that can be removed), whereas ketones are not oxidised under mild conditions. This difference is the basis of the tests that distinguish them. On reduction (for example with hydrogen and a catalyst, or with $LiAlH_4$) aldehydes give primary alcohols and ketones give secondary alcohols.

3.5 Distinguishing Tests

Several simple tests tell aldehydes and ketones apart, all relying on the fact that aldehydes are easily oxidised while ketones are not:

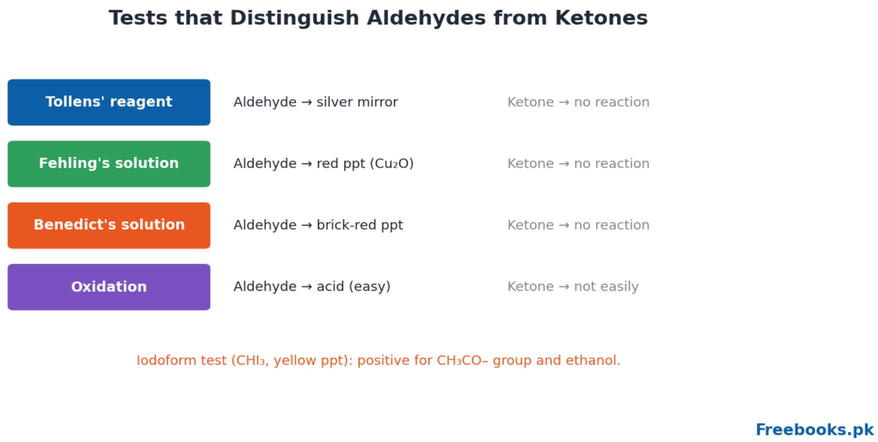

Figure 12.2 — Tests that distinguish aldehydes from ketones.

Key Tests

Tollens' reagent (ammoniacal $AgNO_3$): aldehydes give a bright silver mirror; ketones do not.

Fehling's / Benedict's solution: aldehydes give a red precipitate of Cu_2O; ketones give no reaction.

Iodoform test (I_2/NaOH): a yellow precipitate of iodoform (CHI_3) forms with compounds containing the CH_3CO– group (e.g. acetaldehyde, acetone) and with ethanol.

Teacher's Note

A clean way to explain the tests: they are all mild oxidations. Aldehydes have a hydrogen on the carbonyl carbon and are easily oxidised (positive result); ketones do not, so they are negative — except the iodoform test, which detects the CH_3CO– group in both.

3.6 Uses

Methanal (formaldehyde) is used as a preservative (formalin) and to make Bakelite and other plastics; ethanal is used to make ethanoic acid and other chemicals; and acetone (propanone) is a very common solvent, for example in nail-polish remover and in industry.

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4. Important Definitions

Term	Definition
Carbonyl group	The C=O group present in aldehydes and ketones.
Aldehyde	A compound R–CHO with the carbonyl group at the end of the chain.
Ketone	A compound R–CO–R′ with the carbonyl group between two carbons.
Nucleophilic addition	Addition of a nucleophile across the polar C=O bond.
Tollens' test	Silver-mirror test that is positive for aldehydes.
Iodoform test	A test giving CHI_3 with CH_3CO– compounds and ethanol.

5. Formulas / Rules

Must-Know Facts

Aldehyde R–CHO; ketone R–CO–R′; both contain C=O.

Reactivity: aldehydes > ketones in nucleophilic addition.

Oxidation: aldehyde → carboxylic acid (easy); ketone → not easily.

Reduction: aldehyde → 1° alcohol; ketone → 2° alcohol.

Tests: Tollens' (silver mirror) and Fehling's (red ppt) positive for aldehydes; iodoform for CH_3CO–.

6. Diagrams / Illustrations

Key diagrams for revision:

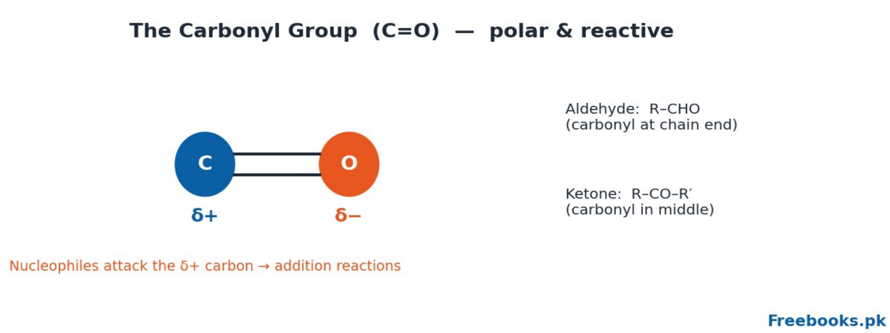

Diagram 1 — The carbonyl group.

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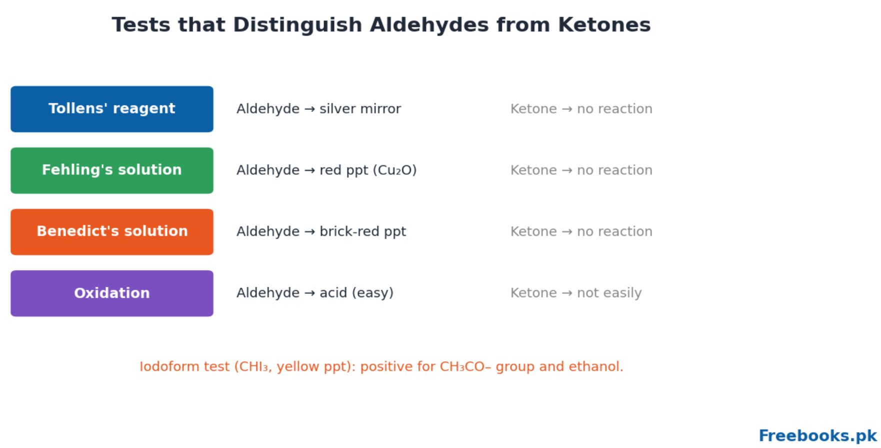

Diagram 2 — Distinguishing tests.

7. Solved Examples

Example 1 — Distinguishing test

Q: How would you distinguish ethanal from propanone?

Solution: Use Tollens' reagent. Ethanal (an aldehyde) gives a silver mirror; propanone (a ketone) does not. Fehling's solution can be used the same way (red precipitate with the aldehyde only).

Example 2 — Reduction

Q: What is formed when propanone is reduced?

Solution: Propanone (a ketone) is reduced to propan-2-ol, a secondary alcohol.

Example 3 — Iodoform test

Q: Which of ethanal and benzaldehyde gives a positive iodoform test?

Solution: Ethanal (CH_3CHO) gives a positive iodoform test because it contains the CH_3CO– group; benzaldehyde (C_6H_5CHO) does not, as it lacks that group.

8. Short Questions

Q1. What is the carbonyl group?
Ans. The C=O group, the functional group of aldehydes and ketones.

Q2. Differentiate an aldehyde from a ketone structurally.
Ans. In an aldehyde the C=O is at the chain end (R–CHO); in a ketone it is between two carbons (R–CO–R′).

Q3. Why is the carbonyl carbon attacked by nucleophiles?
Ans. It is δ+ because oxygen pulls electrons away, so nucleophiles attack it.

Q4. Why are aldehydes more reactive than ketones in addition?
Ans. Ketones have two bulky groups that hinder the nucleophile's approach and stabilise the carbonyl.

Q5. What does Tollens' reagent give with an aldehyde?

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Ans. A bright silver mirror.

Q6. What is formed when a ketone is reduced?
Ans. A secondary alcohol.

Q7. Which functional group gives a positive iodoform test?
Ans. The CH_3CO– (methyl ketone) group, and ethanol.

Q8. Give one use of acetone.
Ans. As a solvent (e.g. nail-polish remover).

9. Long Questions

Q1. Explain the nucleophilic addition reactions of aldehydes and ketones.

Aldehydes and ketones react mainly by nucleophilic addition because their carbonyl group is polar: the carbon is δ+ and the oxygen δ−. A nucleophile attacks the electron-poor carbon, the π-bond of C=O breaks, and the electrons move onto the oxygen to give an alkoxide, which then picks up a proton. In this way hydrogen cyanide adds to give a cyanohydrin, which has one more carbon than the starting compound; sodium hydrogen sulphite adds to give a crystalline bisulphite addition compound that is useful for purifying and identifying aldehydes and some ketones; and a Grignard reagent adds and, after hydrolysis, gives an alcohol (a primary alcohol from methanal, a secondary alcohol from other aldehydes, and a tertiary alcohol from ketones). Aldehydes generally undergo these additions more readily than ketones, because the two carbon groups of a ketone hinder the approaching nucleophile and reduce the positive charge on the carbon.

Q2. Describe the tests used to distinguish aldehydes from ketones.

The key chemical difference between aldehydes and ketones is that aldehydes are easily oxidised while ketones are not, and the distinguishing tests are based on this. In the Tollens' test the compound is warmed with Tollens' reagent (an ammoniacal solution of silver nitrate); an aldehyde reduces the silver ions to metallic silver, which deposits as a bright silver mirror on the tube, whereas a ketone gives no mirror. In the Fehling's test (and the similar Benedict's test) the compound is warmed with a blue copper(II) solution; an aldehyde reduces the copper(II) to a brick-red precipitate of copper(I) oxide, whereas a ketone gives no precipitate. A further useful test is the iodoform test: when a compound containing the CH_3CO– group (such as ethanal or acetone), or ethanol, is warmed with iodine and sodium hydroxide, a yellow precipitate of iodoform (CHI_3) with a characteristic smell is formed. Together these tests allow aldehydes, methyl ketones and other ketones to be identified.

Q3. Compare the reactivity of aldehydes and ketones and explain the difference.

Both aldehydes and ketones react through their carbonyl group, but aldehydes are generally the more reactive of the two, both in nucleophilic addition and in oxidation. There are two main reasons. First, a ketone has two alkyl (or aryl) groups attached to the carbonyl carbon, and these bulky groups get in the way of an approaching nucleophile (a steric effect), whereas an aldehyde has only one such group and a small hydrogen atom. Second, the alkyl groups of a ketone push electron density towards the carbonyl carbon, reducing its δ+ charge and making it less attractive to nucleophiles (an electronic effect). In oxidation the difference is even clearer: the aldehyde's carbonyl carbon carries a hydrogen atom that can be removed, so aldehydes are easily oxidised

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to carboxylic acids, whereas ketones have no such hydrogen and resist mild oxidation. These differences explain why aldehydes give positive Tollens' and Fehling's tests while ketones do not.

10. Multiple Choice Questions (MCQs)

1. The functional group of aldehydes and ketones is:
(A) –OH (B) C=O (C) –COOH (D) –O–

2. An aldehyde has the general formula:
(A) R–CO–R′ (B) R–CHO (C) R–OH (D) R–COOH

3. Tollens' reagent gives a silver mirror with:
(A) ketones (B) aldehydes (C) alcohols (D) ethers

4. Fehling's solution gives a red precipitate of:
(A) Ag (B) Cu_2O (C) CuO (D) Fe_2O_3

5. On reduction a ketone gives a:
(A) 1° alcohol (B) 2° alcohol (C) 3° alcohol (D) acid

6. Aldehydes are more reactive than ketones due to:
(A) resonance only (B) steric and electronic effects (C) hydrogen bonding (D) ionic character

7. A positive iodoform test indicates the group:
(A) –CHO (B) CH_3CO– (C) –COOH (D) –OH only

8. Oxidation of an aldehyde gives a:
(A) ketone (B) carboxylic acid (C) alcohol (D) ester

9. Acetone is commonly used as a:
(A) fuel (B) solvent (C) catalyst (D) fertilizer

10. Which does NOT react with Tollens' reagent?
(A) ethanal (B) methanal (C) propanone (D) benzaldehyde

> **MCQ Answer Key**
> **1-B 2-B 3-B 4-B 5-B 6-B 7-B 8-B 9-B 10-C**

11. Quick Revision / Summary

- Carbonyl C=O: aldehyde R–CHO (end), ketone R–CO–R′ (middle); polar (δ+ C, δ− O).
- Characteristic reaction = nucleophilic addition (HCN, $NaHSO_3$, Grignard).
- Aldehydes more reactive than ketones (steric + electronic).
- Oxidation: aldehyde → acid (easy); ketone → resists.
- Reduction: aldehyde → 1° alcohol; ketone → 2° alcohol.
- Tests: Tollens' (silver mirror), Fehling's (red ppt) for aldehydes; iodoform for CH_3CO–.

12. Exam Tips

> **Teacher's Note**

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Learn the three distinguishing tests and their exact positive results (silver mirror, red ppt, yellow ppt).

State clearly WHY aldehydes are more reactive/easily oxidised (H on carbonyl carbon; steric+electronic).

Know which compounds give the iodoform test (CH_3CO– group and ethanol).

Reduction products: aldehyde → 1° alcohol, ketone → 2° alcohol.

Remember uses: formalin/Bakelite (methanal), solvent (acetone).

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